Attachment A. Machine language translation of EP0325941 performed by European Patent Office web-site.

Method to the preparation of modified polyisocyanates, the polyisocyanates available after this method and their use

The invention relates to a new method to the preparation of Biuret and Uretdiongruppen exhibiting organic polyisocyanates by conversion of excess amounts at (cyclo) aliphatic diisocyanates with a particular amino-alcohol or with its solutions in water and subsequent removal not of the reacted Ausgangsdiisocyanate, as well as the compounds available after this method and their use to the preparation of PU plastics, in particular as isocyanate component in two-component polyurethane lacquers.

The preparation of modified polyisocyanates by conversion of excess amounts at (cyclo) aliphatic diisocyanates, in particular at 1,6-Diisocyanatohexan with Aminoalkoholen is from the DE-OS 2,641,448 already known. With the procedure products of this prior publication it concerns in particular Biuret and urethane-modified polyisocyanates. In the DE-OS 2,641,448 it is also pointed out that the disclosed compounds of byproducts, in particular Trimerisierungsprodukte (isocyanurates), to contain to be able, however on that not more other been received. The presence of Uretdiongruppen in the procedure products of the prior publication is not at all addressed. In accordance with the teaching of the DE-OS to be inferred as from the embodiments viscosities of at least 2400 mPa.s/25 DEG C in all other respects exhibit 2,641,448 using 1,6-Diisocyanatohexan and put out, the modified polyisocyanates prepared as prefered Aminoalkohole. Generally the viscosity of these procedure products lies however still far higher and can reach values of up to 43,000 mPa.s/25 DEG C.

It was now those the invention underlying object, a new method to the preparation of new to put to modified aliphatic polyisocyanates at the disposal whereby the new polyisocyanates should represent stable, comparatively low-viscous liquids, which should exhibit considerable content at dimerisierten isocyanate groups (Uretdiongruppen) beside free isocyanate groups, which with the use of the polyisocyanates as hard ones in two-component polyurethane lacquers as potential, heat-activatable isocyanate groups to be available, whereby the total amount is because of isocyanate groups significant over the content of group of isocyanates of the procedure products mentioned of the state of the art.

This object could become by the provision of the appended more near described invention process dissolved.

Subject-matter of the invention is a method to the preparation of Biuret and Uretdiongruppen exhibiting polyisocyanates by conversion of excess amounts at (cyclo) aliphatic diisocyanates with a modifier with 100 to 210 DEG C and subsequent removal of not reacted Ausgangsdiisocyanat, characterised in that one

(i) as modifiers 1,5-Diaminoheptanol-6 or its solutions in up to 80 mol %, related to solution, water and
(ii) the Ausgangsdiisocyanat in an at least fifteenfold molar excess, related to (i),
used.

Subject-matter of the invention are also the Biuret and Uretdiongruppen of exhibiting polyisocyanates available after this method.

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Subject-matter of the invention is finally also the use of the Biuret and Uretdiongruppen of exhibiting polyisocyanates as isocyanate component with the preparation of PU plastics in the isocyanate polyaddition procedure, in particular as isocyanate component in two-component polyurethane lacquers.

For the invention process suitable Ausgangsdiisocyanate is arbitrary organic diisocyanates with aliphatic and/or cyclo-aliphatic bonded isocyanate groups of the molecular weight range 140 to 300 or their mixtures. Examples are 1,4-Diisocyanatobutan, 1,6-Diisocyanathexahexan, 1,6-Diisocyanato-2,2,4-trimethyl-hexan, 1,12-Diisocyanatododecan, Lysin-C1-C8-alkylester-diisocyanat, 1,3-Diisocyanatocyclobutan, 1,3 - and/or 1,4-Diisocyanatocyclohexan, 3,3 min - Dimethyl-4,4 min - diisocyanatodicyclohexylmethan, 4.4 min - Diisocyanatodicyclohexylmethan, 1-Isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexan or 1,4-Xylylendiisocyanat. Particularly prefered becomes 1,6-Diisocyanatohexan (HDI) as Ausgangsdiisocyanat used.

With the invention-essential amino-alcohol it concerns 1,5-Diaminoheptanol-6 of the formula EM14.1

The preparation of this compound can take place for example such that one converts L lysine in frieier form and/or in its HCl saltform with acetic anhydride in presence of a tertiary organic amine cousin and bottom addition of a 4-Aminopyridin-Derivates in accordance with DE-A 3,425,814 to the 1,5-Diacetaminoheptanon-6. In such a way the available product becomes the 1,5-Diacetaminoheptanol-6 hydrogenated, subsequent by hydrolysis in aqueous mineral acid into the salt of the 1,5-Diaminoheptanol-6 transfered and by treatment with a strong base as free amine 1,5-Diaminoheptanol-6 isolated.

An exemplary embodiment becomes explained on the basis the subsequent formula pattern: EM15.1

In the first step after DE-A the 3,425,814 available 1,5-Bisacetaminoheptanon-6 is subjected in the next step of the actual known hydrogenation of the keto group to the hydroxyl group; for example in waters as solvents using Raney nickels as hydrogenation catalyst with temperatures from approximately 50 to 150 DEG C and an hydrogen pressure from approximately 20 to 50 bar.

The so available aqueous solution of 1,5-Bisacetaminoheptanol-6 becomes, preferably after separation of the catalyst, the direct hydrolysis in acidic solution (in particular in mineral acids) supplied. The 1,5-Bisacetaminoheptanol-6, a solid (Fp.: 105 to 107 DEG C) however also isolated can become.

The subsequent step exists in the actual known hydrolysis (Entacetylierung, cee. DE-A 3,425,814) of the N-acetyl groups in aqueous, mineral-acidic solution to the corresponding, primary amine group contained salts of the 1,5-Diaminoheptanol-6, for example in 4 - to 6 - normal, aqueous hydrochloric acid solution by 4 - to 6 - hour heating bottom reflux conditions. Subsequent restricting and recrystallization lead to cleaned salts of the 1,5-Diaminoheptanol-6. Their conversion with NaOH or KOH from concentrated aqueous solutions leads to the pure, free amine, which however also bottom bypass of the amine salt insulation can become direct with NaOH or KOH as crude amine deposited. An other purification is possible by distillation.

With the invention process 1,5-Diaminoheptanol-6 in substance or in form of an aqueous solution becomes used as modifiers for the Ausgangsdiisocyanat. So for example aqueous solutions of the amino-alcohol with a content of up to 50 mol %, preferably up to 70 mol % waters, can related to the solution, when modifiers become used.

The invention process becomes in the temperature range from 100 to 210 DEG C, preferably 100 to 190 DEG C conducted. At the time of the execution of the invention process at least 15 mole arrives, preferably to 30 to 60 mole diisocyanate at the use per mole of the compounds present in the component (i) (sum of the moles amino-alcohol + the moles waters).

The execution of the invention process can take place for example as follows:

, The aliphatic or cyclo-aliphatic diisocyanate used as starting material becomes in a Rührgefass bottom inert gas atmosphere (e.g. Nitrogen or argon) presented and on 120 to 190 DEG C heated. 1,5-Diamino-6-heptanol becomes, if necessary agitated in form of an aqueous solution, added and the so obtained reaction mixture so long with 120 DEG C to 190 DEG C, until the reaction solution homogeneous is and is the desired refractive index (if necessary in preliminary tests for the respective reaction mixture and the desired in each case content at Uretdiongruppen to specify is) achieved. In this way one receives Biuret, urethane and groups of ISO cyanogen urates exhibiting polyisocyanates with a targeted adjustable content at Uretdiongruppen, as is more detectable <by means of><> the 1 3 C-spectroscopy (see. Angew. Macro mol. Chem. one. 141 (1986) 173-183). The invention process becomes preferably solvent free conducted.

After completion of the reaction the excess Ausgangsdiisocyanat becomes by extraction, for example using n hexane as extracting agent, or preferably by distillation (thin section evaporator) up to a remainder content of max. 1, preferably max. 0.5 Gew. - %, remote.

The procedure products according to invention represent colorless to yellowish colored polyisocyanates liquid with room temperature. They are complete odorless and clearer in solvents inert opposite isocyanate groups such as hydrocarbons, chlorinated hydrocarbons, esters or Ketonen soluble.

The prefered procedure products according to invention on basis of 1,6-Diisocyanatohexan point with 23 DEG C a viscosity from 300 to 5000 mPa.s, to NCO content from 20 to 24 Gew. - % and content at Uretdiongruppen (calculated as C2N2O2) from 4 to 20 Gew. - % up. Beside these groupings are present in the procedure products according to invention Biuret, urethane and isocyanate groups as well as if necessary Allophanatgruppen.

The procedure products according to invention differ from the products of the DE-OS 2,641,440 favourably by a lower viscosity and simultaneous (in particular bottom consideration of the Uretdiongruppen present beside the free isocyanate groups) by a higher NCO functionality and higher NCO content.

The procedure products according to invention represent valuable starting materials to the preparation of PU plastics. In particular they
▲ too are suitable for the preparation of high-quality, light-genuine two-component polyurethane lacquers. In form blocked with blocking agents for isocyanate groups they are suitable also for the preparation of PU baking enamels.

In the subsequent examples relate itself all percentages, as far as nothing different phrased one notes, on weight percentage.

Example 1 (preparation of 1,5-Dimaninoheptanol-6)

a) 1,5-Bisacetaminoheptanon-6

Into a mixture from 3676 g acetic anhydride, 2429 g triethylamine and 2.4 g N, N-Dimethyl-4-amino-pyridin are registered to 1086 g L-lysine-hydrochloride bottom agitation by portion with 40 to 50 DEG C. After approx. 80 l CO2 escaped is, becomes so long with 60 to 70 DEG C after-agitated, to altogether approx. 135 l CO2 cleaved became. One filtered from failed Triethylaminohydrochlorid, the freed filtrate in the vacuo of low portions and the crystallized remaining crude product from ethyl acetate. One receives 1163 g 1,5-Bisacetaminoheptanon-6 from the Fp. 108-110 DEG C.

b) 1,5-Bisacetaminoheptanol-6

In an agitating autoclave 456 g 1,5-Bisacetaminoheptanon-6 in 1,5 l water dissolved and with 50 g became Raney nickel offset. With 90 DEG C and 40 to 50 bar hydrogen pressure agitated becomes up to the end of the absorption of hydrogen. Subsequent one becomes relaxed, by the catalyst filtered and the aqueous solution of 1,5-Bisacetaminoheptanol-6 of the direct acid hydrolysis supplied.

c) 1,5-Diaminoheptanol-6

The aqueous solution from b) becomes with 1,5 kg of 37% of iger hydrochloric acid offset, 6 hours bottom reflux conditions maintained and subsequent in the vacuo of low portions freed. The obtained crude product 1,5-Diaminoheptanol-6-bishydrochlorid becomes subsequent bottom cooling with 480 g 50% of iger sodium hydroxide solution offset. One separates simmering substance obtained from the developed sodium chloride and excess sodium hydroxide solution and cleans the so isolated crude amine, which contains only not-distillable impurities and minor proportions at waters, by distillation in this way can 251 g 1,5-Diaminoheptanol-6 as with 113 to 115 DEG C/0,1 mbar become (yield 86%).
<tb>< TABLE> Columns=4>
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<tb>
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<tb> Head Col 3: H
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<tb>< September> theory< September> 57.5< September> 12.3< September> 19,2
<tb>< September> (related to C7H18N2O)
<tb>< /TABLE>

Example 2 (invention process)

1600 g (10 mole) HDI bottom nitrogen atmosphere on 160 DEG C heated become. To subsequent ones one lets 29,2 g (0.2 mole) zutropfen 1,5-Diaminoheptanol-6 bottom agitation with 160 DEG C during 1 h and to after-agitate 10 minutes with 100 DEG C. The clear solution becomes subsequent so long agitated with 120 DEG C (2 to 6 h), until the refractive index n25_D = 1.4600 is achieved. Subsequent ones one separates the excess HDI by thin section distillation (type "prime route evaporator") with 120 DEG C/0,1 mbar up to a remainder content from 0,1%.
Yield: 370 g
Viscosity: 1000 mPa.s/23 DEG C
NCO content: 23,5 %
Uretdion content: 13 %
Composition after <1>< 3> C-NMR (mol %)1
Biuretgruppen: 51 %; Uretdiongruppen: 33 %;
Groups of ISO cyanogen urates: 16 %.

These indications in "mol %" relate itself here and also in the subsequent examples on the total content of the procedure products at the groups mentioned.

Example 3

2520 g (15 mole) HDI become bottom nitrogen atmosphere on 160 DEG C heated and within 1 h with 43,8 g (0.3 mole) 1,5-Diaminoheptanol-6 bottom agitations offset. One agitates 1 h with 160 DEG C after, cools on 120 DEG C and agitates so long with this temperature, until the refractive index n25_D = 1.4610 is achieved (2 to 3 h). After workup in accordance with example 2 one receives a product with the subsequent data:
Yield: 851 g
Viscosity: 1700 mPa.s/23 DEG C
NCO content: 23,7 %
Uretdion content: 12 %
Composition after <1>< 3> C-NMR (mol %)1
Biuretgruppen: 48,8 %; Uretdiongruppen: 30,5 %;
Groups of ISO cyanogen urates: 20,7 %.

Example 4

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In accordance with example 2 1512 g (9 mole) become HDI and 43,8 g (0.3 mole) 1,5-Diaminoheptanol-6 the conversion brought. After reaching the refractive index n25_D = 1.4750 the product corresponding is regenerated.
Yield: 675 g
Viscosity: 6200 mPa.s/23 DEG C
NCO content: 21,9 %
Uretdion content: 8 %
Composition after <1>< 3> C-NMR (mol %)1
Biuretgruppen: 31,0 %; Uretdiongruppen: 14,2 %;
Groups of ISO cyanogen urates: 54,8 %.

Example 5

In accordance with example 2 1680 g (10 mole) become HDI and a solution from 21,9 g (0.15 mole) 1,5-Diaminoheptanol-6/2,7 g (0.15 mole) water the convention brought. One agitates 1 h with 100 DEG C after and leaves the clear solution subsequent so long with 120 DEG C (1 to 3 h) to the refractive index n25_D = 1.4620 achieved is. After workup one receives a product with the data:
Yield: 372 g
Viscosity: 1200 mPa.s/23 DEG C
NCO content: 23,0 %
Uretdion content: 11 %
Composition after <1>< 3> C-NMR (mol %)1
Biuretgruppen: 48,5 %; Uretdiongruppen: 27 %;

Groups of ISO cyanogen urates: 24,5 %.

Example 6

In accordance with example 2 1600 g (10 mole) become HDI and a solution from 29,2 g (0.2 mole) 1,5-Diaminoheptanol-6/1,0 g (0.1 mole) water the conversion brought. After reaching a refractive index n25_D = 1.4615 in accordance with example 2 one regenerates.
Yield: 375 g
Viscosity: 2700 mPa.s/23 DEG C
NCO content: 23,8 %
Uretdion content: 0 %
Composition after <1>< 3> C-NMR (mol %):
Biuretgruppen: 57,9%, Uretdiongruppen: 18,3 %;
Isocyanuratgruppen: 23,8 %.

Example 7

In accordance with example 6 1600 g (10 mole) become HDI and a solution from 18,25 g (0.125 mole) 1,5-Diaminoheptanol-6/2,25 g (0.125 mole) water the conversion brought. After reaching a refractive index n25_D = 1.4588 in accordance with example 6 one regenerates.
Yield: 299 g
Viscosity: 980 mPas/23 DEG C
NCO content: 24,3 %
Uretdion content: 10 %
Composition after <1>< 3> C-NMR (mol %):
Biuretgruppen: 66,1 %; Uretdiongruppen 21.2%;
Isocyanuratgruppen 12.7%.

Example 8 (use according to invention)

The polyisocyanate from example 7 becomes a 2-components pur-paint processed, by becoming combined with a hydroxyl component A, which represents the mixture of a polyester with a Hydroxypolyacrylat.

To the preparation of the hydroxyl component A one proceeds as follows:

280 parts by weight of a polyester from 2,5 mole trimethylolpropane, 1.65 mole Phthalsureanhydrid, 0.6 mole adipic acid and 1.15 mole 2-Ethylhexansaure are merged in solution with 350 parts by weight of a polymer from 39,63 mol % styrene, 28.01 mol % n-butyl acrylate, 9.94 mol % acrylic acid and 31.42 mol % hydroxyethyl methacrylate. The mixture is 65% industrial union in xylene/butyl acetate (weight ratio (1: 3) dissolved. The solution has an hydroxyl number of 95.

The polyisocyanate is unpigmentiert and pigmented with the hydroxyl component A (with titanis of the rutile type, over a three-rolling mixer the incorporated becomes and in the finished lacquer in an amount of approx. 80 Gew. - Parts per 100 Gew. - Parts at PU-formed starting materials,) in the NCO/OH ratio 1:1 mixed is contained. With Methoxypropylacetat adjusted becomes (according to DIN 53,211,4 mm) on a spraying viscosity of 18 seconds. The sprayingfinished lacquer solution becomes on river steel plates injected and bottom various conditions cured (see. subsequent table).
<tb>< TABLE> Id=Tabelle Columns=3 OR=L
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<tb> Head Col 3: pigmented
<tb> solid content with spraying viscosity 18< September> 54%< September> 62%
<tb> processing time< September> 3.7 h< September> 10.6 h
<tb>
<tb> SubHead Col 1: Pendulum-hard (s) (according to DIN 53,157) after cure
▲ top <tb> 30 min/80 DEG C< September> 179< September> 195
<tb> 30 min/120 DEG C< September> 210< September> 194
<tb> 30 min/80 DEG C + 16 h/60 DEG C< September> 210< September> 198
<tb> 7 days with approx. 23 DEG C< SEPTEMBER> 204< SEPTEMBER> 187
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<tb> SubHead Col 2: Lösemittelbeständigkeit* after
<tb> 30 min/120 DEG C and aging< September> 0.0.0.1< September> 0,0,0,1
<tb> 7 days with approx. 23 DEG C
<tb>< /TABLE>

Explanations of the table:
* Solvent stability

The Anlöslichkeit of the paint films becomes judged after 1 min impact time of the solvents. The damage of the paint film becomes in 6 hours judged of
0 = paint film is complete unchanged to
5 = paint film dissolves.

In the indicated order the subsequent solvents come to the application:
Toluene
Methoxypropylacetat
Ethyl acetate

Acetone